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THE ROLE OF THE ASH CONSTITUENTS OF COKE IN GRAPHITIZATION

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The process of the graphitization of coal includes the stages: 1) thermic recrystallization (development of graphite crystals); 2) formation and disintegration of carbides, formed from ash constituents; and 3) thermic refining of coal. The first process is the principle one. The other two are secondary but should not be neglected as will be made clear in the text of this article.

The chief factors contributing to the success of thermal recrystallization are favorable conditions of contact of the crystalline carbon grains, temperature and time. In spite of indications that thermal recrystallization of carbon should proceed at a temperature somewhat higher than 1,400°C, the work of many authors shows that for anthracites this temperature is not lower than 2,300°C, and for petroleum coke, 2,250°C. In proportion to the rise of the temperature, the recrystallization of graphite is intensified therefore it is possible for successful recrystallization of graphite to admit a temperature equal to 2,600°C. In practice, attainment of such a high temperature encounters great difficulties. In addition, the temperature of the pocket of graphitized electrodes in the oven is not distributed uniformly. This is illustrated by Table 1 where the results of measurement of temperatures by oven zones are given.

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Table 1

Time From Start of Heating (in Hours)	Center of Electrodes	Temperature in Degrees C Face of Electrodes	Beneath Electrodes
44	1,400	1,200	1,400
60	2,130	1,800	2,300 (Shut-down of oven)
68	2,050	1,950	2,300
76	1,880	1,930	2,100

Thus, in carrying out graphitization in the Acheson-type oven, generally used for this purpose, it is necessary to stop at a temperature not exceeding 2,300°C (which is lower than the temperature of 2,460°C recommended by Arndt). At this temperature recrystallization can proceed successfully in case of a good contact between the carbon crystals at the time of their proper orientation and in the absence of retarding factors ("layers of impurities," according to Tammann), rendering the movement of the ions difficult.

Foreign mineral bodies in coal (ashes) may show both a detrimental and a beneficial activity, depending on their composition with the formation and disintegration of the carbides taking place on the one hand, and thermal refining on the other. Hitherto various authors have not been absolutely clear on this question, and even the latest works of V. S. Veselovskiy do not indicate what influence foreign bodies have on the structure of the graphite produced, not to mention the fact that the data adduced by him on the influence of foreign bodies is very questionable and contradictory, which makes his conclusion very unreliable, i.e., "for refining, a rise in temperature to somewhat above 2,200°C is necessary;" (1) It is well known that the loss of ash by the material, even at a temperature of 3,000°C, is not complete; and that in proportion to the decrease in ash content, the temperature for refining must increase sharply. Mirani's data are quoted in Table 2.

Table 2

Temperature (in °C)	500	1,800	2,200	2,700	3,000
Ash Content (%)	1	0.66	0.36	0.2	0.07

The foreign bodies, contained in the coal ash, behave differently during graphitization. The elasticity of dissociation of the chief ash constituents in millimeters on a mercury column at one atmosphere is shown in Table 3.

Table 3

t (°C)	$\lg \text{Po}_2/\text{Fe}_2\text{N}_3$	$\lg \text{Po}_2/\text{FeO}$	$\lg \text{Po}_2/\text{SiO}_2$	$\lg \text{Po}_2/\text{Al}_2\text{O}_3$	$\lg \text{Po}_2/\text{C}_2\text{O}$	$\lg \text{Po}_2/\text{CO}$
1000	-4	-14.7	-25.5	-33.3	-	-19.0
1500	-10.9	-8.4	-16.0	-20.5	-25.0	-16.5

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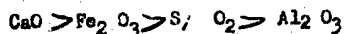
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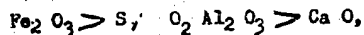
The data of Table 3 shows that in the reduction by carbon the elasticity of dissociation diminishes successively in the series: ferric oxide, ferrous oxide, silica, alumina, calcium oxide. Reduced metals form carbides and are volatilized very differently in the disintegration of the latter, because of the extreme difference in their boiling points. The boiling point of iron at one atmosphere is 3,235°C; silicon 2,400°C; aluminum 1,800°C; and calcium 1,430°C.

The data adduced show that in thermal refining, iron is the most difficult to volatilize. While it is well known that better foreign graphites, produced in the same Acheson ovens, have a low ash content, foreign firms point out the possibility of their more complete refinement in case of necessity. Thus, at practically the same temperatures foreign firms produce graphite with a lower ash content, and even with no ash content. It is found that the possibility of producing graphite with a small ash content lies in the initial iron content and the original coal. We verified this by combustion of better foreign and domestic graphites. While the ashes of our graphites were highly ferrous (deep brown), the ashes of the better graphites of the Acheson firm were entirely free from iron (pure white). This means that the better foreign graphites contain practically no iron. The harmful influence of iron lies in the fact that it forms alloys with aluminum and silicon which are stable at high temperatures. Thus thermal refining from aluminum and silicon is impeded.

Foreign bodies, however, affect the properties of graphite in a more complex manner: thus, for instance, better graphites for electrical conductivity are produced by the introduction of CaO and Fe_2O_3 and the poorest graphites by the introduction of Al_2O_3 . The following series obtains in order of the deterioration of the electrical conductivity of graphite:



At the ignition point (taking into account the fact that the higher it is the more completely graphitization proceeds) the following series obtains in the order of deterioration:



which explains the diversity shown in the introduction of foreign bodies during graphitization.

It is necessary to take into consideration the fact that the thermal refining of coal is not some "independent" process, but is closely linked with the process of graphitization, and the temperature of the thermal refining, especially for the eliminations of iron vapors, must be very high. Finally, the thermal refining proceeds selectively, in the long run, i.e., not all the foreign ash bodies are evaporated in equal measure and the composition of the final ash varies.

According to our assumptions, the elimination of iron should be the most difficult of all, and thermal refining to the point of complete elimination of iron would require practically unrealizable temperatures, i.e., iron will always set the limit for the final ash content of graphite.

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The simplest calculations, according to Raoult's law, show that under ordinary conditions, the vapor tension of silicon on fusion decreases 0.82 times, which raises the boiling point approximately 150°C, i.e., the evaporation of silicon is impeded by the presence of an excess of iron. The case of aluminum is analogous. Here, under the same circumstances, the vapor tension is decreased by 0.814, which raises the boiling point approximately 100°C. Thus, the difficulty of eliminating iron impedes the elimination of silicon and aluminum.

In order to show how silicon, iron, and aluminum affect the development of graphite crystals (graphitization), we took Debye crystallograms from graphitized pitch coke at a temperature of 2,300°C:

Figure 1 shows the poor crystal structure of the given coke with an 0.8 percent ash content; Figure 2 shows graphitized coke to which, before coking, a 5 percent admixture of silicon dioxide was added; Figure 3, the same but with an admixture of Fe_2O_3 ; and Figure 4, with an admixture of Al_2O_3 . The conditions of graphitization and the quantity of the admixture are the same. It is evident that, when SiO_2 was added the best crystallization of graphite was obtained; somewhat poorer crystallization was evidenced when Fe_2O_3 was added, and still poorer crystallization with the addition of Al_2O_3 .

If conditions for eliminating aluminum are created, the structure of the graphite is improved, as shown in Figure 5. However, in order to eliminate aluminum easily, the presence of iron is necessary since the formation of aluminum carbide will then take place at 2,175° K (when $P_{\text{CO}}=1\text{-atm}$) and disintegration of aluminum carbide, according to Arndt, takes place at 2,273-2,375° K (or, according to Ruff somewhat more than 2,473° K).

The solution to the problem of eliminating iron from the ashes of coal for the purpose of graphitization is arrived at easily by chlorination, as shown by the work of V. Spitsyn. (3)

We quote his data on losses of foreign bodies in coal after one hour under the action of chlorine (rate of gas stream one liter per hour) in relation to the temperature:

At Degrees C		Losses From Initial Quantity (in %)
Fe_2O_3	400	92.47
	600	0
Al_2O_3	800	2.08
	1,000	86.15
SiO_2	1,000	0.7--1.0

Fe_2O_3 is eliminated most effectively, followed by Al_2O_3 . SiO_2 is completely eliminated in the thermal refining. Thus, by using chlorination before graphitization, it is possible to obtain graphite absolutely free from ash.

Calcium oxide forms carbide after reduction, which dissociates at temperatures not lower than 2,500°C and evaporates. Calcium does not produce alloys with iron, and, therefore, its elimination encounters no difficulties during hot operation of the oven (2,500 - 2,600°C).

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CONCLUSIONS

1. The ash content of the graphite obtained is limited by the iron in the ash of the original coal.

2. To obtain graphite without ash content it is necessary to eliminate the iron by preliminary treatment, since by virtue of its high boiling point, it is retained in the graphite and, by forming stable alloys with silicon and aluminum, impedes the elimination of these constituents.

3. The greatest contributor to the crystalline structure of synthetic graphite is SiO_2 ; (however, the temperature of the process must not be lower than $2,300 - 2,400^\circ\text{C}$ for complete disintegration of the carborundum).

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